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(74) Agent: MARKS & CLERK; Alpha Tower, Suffolk Street  
Queensway, Birmingham B1 1TT (GB).

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(71) Applicant (for all designated States except US):  
AD.SURF.ENG. [GB/GB]; Birmingham Research Park, Vincent Drive, Birmingham B15 2SQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BELL, Thomas [GB/GB]; St. Mawes, 1 Mariners Road, Blundellsands, Merseyside L23 6SX (GB). DONG, Hanshan [GB/GB]; 88 Gibbins Road, Selly Oak, Birmingham B29 6QP (GB). LI, Chenxi [CN/GB]; 39 Hobson Road, Selly Park, Birmingham B29 7QP (GB).



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(54) Title: SURFACE TREATMENT OF CO-CR BASED ALLOYS USING PLASMA CARBURIZATION

(57) Abstract: The present invention relates to a method of modifying a surface characteristic (eg. wear resistance and/or corrosion resistance) of a cobalt-chromium based alloy article. The method comprises plasma treating the article at a temperature in the range of from 300 to 700 °C and at a pressure of from 100 to 1500 Pa for 1 to 50 hours in an atmosphere comprising at least one carbon-containing gas, whereby to introduce carbon into a surface region of said article. The present invention also resides in a surface-hardened cobalt-chromium based article producible by the method of the invention. The article is characterised by having a surface region comprising a supersaturated solid solution of carbon in cobalt or a surface region comprising a supersaturated solid solution of carbon in cobalt and chromium carbides. Surface hardened articles producible by the method of the invention include medical implants and engineering components.

## SURFACE TREATMENT OF CO-CR BASED ALLOYS USING PLASMA CARBURIZATION.

The present invention relates to a process for producing a superior wear-resistant surface on cobalt-chromium (Co-Cr) based alloy articles.

Particularly but not exclusively, it relates to a surface hardening process applicable to cobalt-chromium (Co-Cr) based metal-on-metal orthopaedic implant devices (prostheses), wherein surface hardness and wear resistant properties of the prostheses are enhanced without loss of corrosion resistance.

Cobalt-chromium based alloys have typically been used for orthopaedic applications because of their strength, resistance to wear and corrosion and biocompatibility. However, under conditions of sliding wear or articulation of the Co-Cr alloy against other bearing surfaces (particularly, ceramics or Co-Cr alloy counterfaces), the cobalt-chromium alloy produces wear debris from the counterface surfaces in relative motion. This raises a major concern over the carcinogenic effect of such Co-Cr wear debris and the release of such metal ions as Co and Cr. Therefore, the surface of the Co-Cr alloys must be hardened in order to minimise wear, thus leading to long-life Co-Cr orthopaedic prostheses. Several methods for improving wear resistance of Co-Cr based alloys and such articles made from these alloys have been attempted.

One approach to enhancing the wear performance of metallic femoral components (hip and knee prostheses) is to coat their surfaces with such ceramic coatings as TiN (J.A. Davidson, Ceramics in substitutive and reconstructive surgery (P. Vincenzini ed), Elsevier, Amsterdam, 1991 pp157-166) and more recently diamond-like carbon (DLC) coating (M.

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Allen, *J. Biomed. Mater. Res.*, 58(2001), pp319-328). Potential drawbacks to this approach are concerns over spallation of coatings (M.T. Raimondi and R. Pietrabissa, *Biomaterials*, 21(2000), pp907-913) due to the non-metallurgical bonding and galvanic corrosion (caused by the large galvanic potential difference and pinholes in coatings) (R.S. Lillard et. al., *Surface Engineering* 15 (1999), pp221-224). Although a TiN coating has been explored for use as a bearing surface against UHMWPE since the late 1980's, laboratory testing and clinical results have been limited. Indeed, it was reported in 1998 that 5,000 hip operations might have to be repeated in the UK, the problem being attributed to the TiN-coated surface (R. Ellis et. al., *The Times*, 19 February 1998, p1.). Although simple configuration laboratory tests indicated that the DLC coatings had exceptional friction and wear characteristics, tests on hip simulators produced early failures of the coatings (A.H.S. Jones and D. Teer 'Friction and wear testing of DLC type coatings on total hip replacement prostheses' Seminar on The Friction Lubrication and Wear of Artificial Joints – Tribology Meets Medical, Institute of Mechanical Engineers, 30 November 2000, Leeds). Clearly there is cause for concern in using coatings for metallic femoral components. The problem is mainly due to the formation of an oxide scale ( $\text{Cr}_2\text{O}_3$ ) on the alloy surface due to the strong affinity of chromium, which is a major alloying element of Cr-Co alloys, with oxygen in air. This oxide scale frequently cause a poor adhesion between a coating and the Co-Cr alloy surface. Surface treatment of Co-Cr alloys usually has to overcome this major problem, and consequently, such coating techniques as PVD coating, electroplating, and electrolysis plating have limitations for Co-Cr alloys, as compared with coating and plating for most ferrous alloys.

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Another approach to improving the wear performance of femoral components is to modify the metallic surface. In this respect, ion implantation with nitrogen has been employed since the mid 1980's to improve wear resistance of metallic bearing surfaces made of Ti-6Al-4V, 316L and Co-Cr-Mo (J.I. Onate, Surface and Coatings Technology, 142-144 (2001), pp1056-1062). However, it should be noted that the effectiveness of ion implantation in enhancing wear resistance of Co-Cr-Mo alloys for metal-on-metal articulation is limited by the inherent line-of-sight nature of the ion beam and the very thin modified layer which is produced. It is difficult, if not impossible, to produce a homogeneous surface modified layer on 3-D complexly shaped prostheses using the line-of-sight ion beams. In addition, the thickness of the modified surface layer (normally in the range of 0.01 to 0.2  $\mu\text{m}$ ) is far less than the average annual linear wear rate of Co-Cr-Mo prostheses.

In addition to ion implantation with nitrogen, known surface-hardening methods include gas nitriding or plasma nitriding. A nitriding process is disclosed in detail in US Patent No. 5,912,323 issued on May 3 1994 entitled "METHOD OF SURFACE HARDENING COBALT-CHROMIUM ALLOYS FOR ORTHOPAEDIC IMPLANT DEVICES", which disclosure is hereby incorporated by reference. To produce a measurable hardened layer, a treatment duration as long as 48 hours needs to be used. The thickness of the effectively hardened layer is very small as evidenced by the statement that "the peak nitrogen concentration occurs at a depth between 10 and 100nm". This is largely due to the strong affinity between nitrogen and chromium. Indeed, it was found that after plasma nitriding at 550°C for 8h in a 75%N<sub>2</sub>-25%H<sub>2</sub> gas mixture, only a

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compound layer of CrN was observed in the nitrided case of Stellite 6B, a Co-30Cr alloy without the formation of an appreciable diffusion zone (P.H. Howill, Ion nitriding stellite in T. Spaluins and W.L. Kovaes (eds): Proceedings of 2<sup>nd</sup> International Conference of Ion Nitriding/Carburising. ASM International 1990, 175-176).

It is an object of the present invention to provide an improved method of treatment of Co-Cr based alloy articles, which can enable the above-mentioned disadvantages to be obviated or mitigated.

In general, the present invention provides an improved surface hardening process which is relatively cost-effective and which is capable of producing, at a relatively low temperature, combined improvement in wear and corrosion resistance of Co-Cr based alloy joint prostheses (such as hip and knee joints) and producing highly wear-resistant Co-Cr based alloy engineering components (such as valves and tools) without undue loss in corrosion resistance.

According to the present invention, there is provided a method of modifying a surface characteristic of a cobalt-chromium based alloy article, comprising plasma treating the article at a temperature in the range of from 300 to 700°C and at a pressure of from 100 to 1500 Pa for 1 to 50 hours in an atmosphere comprising at least one carbon-containing gas, whereby to introduce carbon into a surface region of said article.

The surface characteristic to be modified by the method of the present invention may be any one or more of hardness, wear resistance, corrosion resistance and fatigue strength.

Preferably, said article is a medical implant, such as a joint or knee prosthesis, in which case said plasma treating is preferably carried out at a temperature in the range of from 350 to 550°C, and more preferably 400 to 500°C. At these temperatures, the method generally increases wear resistance and corrosion resistance.

Alternatively, said article may be an engineering component, such as a knife, valve, blades or shaft, in which case said plasma treating is preferably carried out at a temperature in the range of from 450 to 700°C, more preferably 600 to 650°C. At these temperatures, the method generally increase wear resistance, but not necessarily corrosion resistance.

Preferably, said treatment pressure is in the range of from 400 to 600 Pa and is more preferably about 500 Pa.

Preferably, the duration of said treatment is in the range of from 2 to 50 hours and more preferably 5 to 30 hours.

Preferably, the or each carbon-containing gas is selected from a hydrocarbon (eg. methane), carbon dioxide and carbon monoxide.

Preferably, the plasma treatment is carried out in the presence of at least one unreactive gas, for example selected from hydrogen, helium, argon or other noble gas. As used herein "unreactive" relates to a gas which does not become incorporated into the article to any significant extent.

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Preferably, the plasma treatment is carried out in the presence of at least one reactive gas, such as a nitrogen containing gas (eg. N<sub>2</sub> or ammonia). As used herein "reactive" relates to a gas which (or a part of which) does become incorporated into the article to a certain extent. Where a nitrogen-containing gas is used, the plasma treating step is preferably effected at a temperature of from 300 to 500°C.

Particularly preferred gas mixtures are hydrogen and methane, and hydrogen, argon and methane.

Preferably, the or each carbon-containing gas constitutes from 0.5 to 20% by volume of the total atmosphere. Preferably, said reactive gas (when present) constitutes from 0.5 to 10% by volume of the total atmosphere.

Preferably, said plasma treatment is effected in the absence of oxygen.

The method may include an article cleaning step prior to the plasma treatment step to remove any oxide scale. Preferably, said cleaning is effected by sputter cleaning (i.e. bombardment of the article surface with positive ions). Said cleaning step may be effected at or below the plasma treatment temperature in an atmosphere of one or more of gases selected from hydrogen, helium, argon or other noble gas.

It will be understood that after plasma treating, the article will be cooled. The rate of cooling may be anything from 0.1°C/min up to 1000°C/min. Cooling may be achieved by slow cooling in the plasma treating atmosphere or by fast cooling by quenching in a liquid. In order to

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prevent dimension distortion and oxidation, slow cooling in the plasma treating atmosphere is preferred.

Particularly for medical implants, a passivation and/or polishing step may be desirable after completion of the plasma treatment.

The present invention also resides in a surface-hardened cobalt-chromium based article producible by the method of the present invention, said article characterised by having:-

- (i) a surface region comprising a supersaturated solid solution of carbon in cobalt or,
- (ii) a surface region comprising a supersaturated solid solution of carbon in cobalt and chromium carbides.

Preferably, said surface region has a thickness in the range of from 3 to 50  $\mu\text{m}$ .

The nature of the Co-Cr based alloy is not particularly limited, and for example, any other alloying ingredients such as molybdenum, nickel, tungsten and titanium may be included in the alloy composition. Carbon may also be included, preferably in the range of from 0.04 to 1.6wt%, more preferably in the range of 0.04 to 0.4wt% in the case of a medical implant, and 0.4 to 1.6wt% in the case of an engineering component.

Among the Co-Cr based alloys which are useful for joint prostheses are ASTM F75 (ISO5832/4), ASTM F799 (ISO5832/12), ASTM F90 (ISO5832/5) and ASTM F562 (ISO5832/6) or their equivalents with different trade names. Articles formed of these alloys which can be

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surface treated at a relatively low temperature (300-500°C) in accordance with the present invention include conventional hip and knee joint prostheses, metal-on-metal advanced bone conservation prostheses, dental implants and other implant devices. Among the Co-Cr based alloys which are useful for wear and/or corrosion resistant engineering components are Stellite 6B, Stellite 6K, MP35N and Ultimet. Wear-resistant engineering components made of these Co-Cr based alloys which can be surface treated at a relatively high temperature (600-700°C) in accordance with the present invention include knives and blades for chemical and food processing industrials, valves and pumps in the chemical and power industrials, bushings and steel mill equipment. Among the Co-Cr based alloys which are useful for hardfacing deposits are the Stellite family (more than 20 alloys) and ERCoCr alloys (ERCoCr-A, -B, -C or -E). Articles deposited with these hardfacing alloys which are preferably surface treated at a relatively high temperature (300-700°C) in accordance with the present invention include valves, dies, punches, moulds, turbine blades and knifes.

Embodiments of the present invention will now be described by way of example only, with reference to the accompanying drawings in which:-

Fig 1 is a schematic view of a dc plasma unit in which the treatment described in the preferred embodiments below was effected,

Fig 2 is a micrograph of the cross-sectional microstructure of a Co-Cr-Mo test piece treated in accordance with the present invention,

Fig 3 shows XRD patterns for untreated test pieces and test pieces surface hardened in accordance with the present invention, and

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Figs 4-6 are graphs showing the properties of untreated test pieces and test pieces surface hardened in accordance with the present invention.

Typical examples of suitable Co-Cr based alloys which are susceptible to the process of the present invention are summarised in Table 1. The Co-Cr based alloys of which the article is formed may be in the wrought, cast, hardfacing deposit or PM/HIP form before the article is subjected to the process to the present invention.

TABLE 1: Examples of useful Co-Cr based alloys

Alloy	Cr	Mo	Ni	W	C	Ti	Co
<i>Wear-corrosion resistant biomedical alloys</i>							
F75 (ISO5832/4)	27-30	5-7	<1	-	<0.35	-	bal
F799 (ISO5832/12)	26-30	5-7	<1	-	<0.35	-	bal
F90 (ISO5832/5)	19-21	-	9-11	14-16	<0.15	-	bal
F562 (ISO5832/6)	19-21	9-11	33-37	-	<0.15	<1	bal
<i>Wear-resistant alloys</i>							
Alloy 6B	28-32	<1.5	<2.5	3-5	0.8-1.2	-	bal
Alloy 6K	28-32	<1.5	<2.5	3.5-5.5	1.5-1.7	-	bal
<i>Corrosion-resistant alloys</i>							
MP35N	19-21	9-11	34-36	-	-	-	bal
Ultimet	25-27	4-6	8-10	1-3	<0.06	-	bal
<i>Hardfacing alloys</i>							
ERCoCr-A	~28	-	-	~5	~1.2	-	bal
ERCoCr-B	~29	-	-	~8	~1.5	-	bal
ERCoCr-C	~31	-	-	~13	~2.5	-	bal
ERCoCr-E	~27	~6	-	~8	~0.2	-	bal

The surface-treatment-process can be applied as a final procedure without causing deterioration of the properties of the substrate or dimensional distortion of the article. Articles for which the process of the present invention is suitable include such articles as ferrules, valves, gears and shafts. There is no particular limit in the size of articles that can be treated using the process of the present invention.

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In order to demonstrate the advantages of the present invention, a series of Co-Cr based alloys (Table 2) were treated in accordance with the present invention.

In the Examples, surface treatment was carried out using a dc plasma nitriding apparatus shown in figure 1. The apparatus comprises a sealable vessel 10, a vacuum system 12 with a rotary pump (not shown), a dc power supply and control unit 14, a gas supply system 16, a temperature measurement and control system 18 including a thermocouple 24, and a work table 20 for supporting articles 22 to be treated.

TABLE 2: Alloy composition of the Examples

Sample designation*	Condition	Composition (% by wt)
A	Wrought	Co-27.6Cr-5.5Mo-0.06C
B	Wrought	Co-37.4Cr-6.1Mo-0.19C
C	Cast (MMT)	Co-29.2Cr-6.1Mo-0.21C
D	Cast (DEP)	Co-27.2Cr-0.17C
E	Cast (DRILL)	Co-29.6Cr-5.9Mo-0.05C
F	PM/HIP	Co-28.2Cr-5.8Mo-0.04C

\*For each sample designation, a different sample was treated at 400, 500 and 600°C (designated A400, A500, A600 etc.)

The articles 22 to be treated were Co-Cr based alloy discs 25mm in diameter and 8 mm in thickness. The discs were placed on the table 20 inside the vessel 10. The table 20 was connected as a cathode to the power supply and control unit 14, and the wall of the vessel 10 was connected to the dc source as the anode. The temperature of the discs 22 was measured by the thermocouple 24 inserted into a hole of 3 mm diameter drilled in one of the discs 22 or a dummy sample. After the

sealable vessel 10 was tightly closed, the rotary pump was used to remove the residual air (oxygen) and thus reduce the pressure in the vessel. When the reduction in pressure reached 10 Pa (0.1 mbar) or less, a glow discharge was introduced between the article 22 (cathode) and the vessel wall (anode) by applying a voltage of 400 volts to 900 volts between these two electrodes. A heating gas of hydrogen was at the same time introduced into the vessel 10. The pressure of the hydrogen gas in the vessel 10 was increased gradually as the temperature of the articles 22 increased. No external or auxiliary heating was employed, and the articles 22 were heated by the glow discharge only.

In other embodiments (not shown), an external heater attached to the vessel may be employed, or a combination of external heating and electrical glow discharge heating may be employed. Direct current (dc) discharge, pulsed dc discharge or alternating current (ac) discharge may be used.

After the articles 22 were heated to the prescribed temperature, a gas mixture of hydrogen (98.5%) and methane (1.5%) was introduced into the vessel 10 and the plasma treatment started. Treatment temperatures from 400°C to 600°C were employed for a treatment time of 10 hours. The working pressure in the treatment step was 500 Pa (5.0 mbar) for all the Examples.

During the plasma heat treatment, the methane is ionised, activated and dissociated to produce carbon ions and activated carbon atoms and neutral molecules, which then diffuse into the surface of the disc forming a carbon diffusion layer. When the plasma treatment is carried out at a relatively low temperature ranging from 300 to 550°C, the carbon atoms

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mainly reside in the cobalt lattices, forming a supersaturated solid solution with a possible nanocrystalline structure due to the relatively low temperatures employed in the treatment. The resultant layer has a high hardness, good fatigue strength and excellent wear and corrosion resistance (see below). When the plasma treatment is carried out at a relatively high temperature ranging from 600 to 700°C, the carbon atoms partially reside in the cobalt lattices forming a supersaturated solid solution and partially combined with carbon forming chromium carbides. The resultant layer has a high hardness, fatigue strength and excellent wear resistance.

After the completion of the plasma treatment, the glow discharge was turned off and the articles 22 were allowed to cool in the vessel 10 in the treatment atmosphere down to room temperature before they were removed from the vessel.

The articles 22 were then subjected to X-ray diffraction analysis for phase identification, glow discharge spectrometry (GDS) analysis for chemical composition determination, surface hardness measurements, metallography analysis of the cross section, electrochemical corrosion tests and wear tests.

A typical micrograph showing the cross-section of the carburised sample is given in figure 2. The sample was electrolytically etched in a 10% H<sub>2</sub>SO<sub>4</sub> water solution. It can be seen that the carburised specimen is characterised by an "un-etched layer" on the surface followed by a carbon diffusion layer ("case") beneath and the heavily etched substrate ("core"). The un-etched layer is dense, no details can be revealed even under high

resolution FEG-SEM. The thickness of the total carburised case depth increases with increasing carburising temperature. In conjunction with the chemical composition analysis, the case depth was determined to be 3.1, 9.3 and 20.2  $\mu\text{m}$  respectively for the A-sample treated at 400°C, 500°C and 600°C for 10 hours.

Figure 3 shows the XRD patterns for the untreated and carburised Co-27.6Cr-5.5Mo-0.06C alloy (Sample A). As can be seen, the untreated alloy consists of a mixture of f.c.c. structured  $\gamma$ -Co and h.c.p. structured  $\epsilon$ -Co. It can be deduced from the height of the XRD peaks that the untreated alloy contains mainly  $\gamma$  with a small amount of  $\epsilon$ . Plasma carburising has changed the phase constituent in the alloy surface. As shown in figure 3, only two main diffraction peaks at lower angles and some minor peaks at higher angles are detected. These peaks could not be matched to either  $\gamma$ -Co,  $\epsilon$ -Co or any other phases given in the existing Powder Diffraction Database. However, they exhibit the same characteristics as those generated by the S-phase in plasma nitrided or carburised stainless steel (Y. Sun X. Li and T. Bell *Surface Engineering*, 1999, Vol 15, No. 1, pp49-54). It thus follows that S-phase was indeed produced in the plasma carburised Co-Cr-Mo alloy surface. The two main S-phase peaks, indicated as S(111) and S(200), correspond to the  $\gamma$  (111) and  $\gamma$  (200) of the substrate but are at lower angles. It is thought that the peak shift is caused by the solution of carbon which expands the f.c.c lattice structure of the substrate.

The surface mechanical properties of the plasma carburised samples were assessed using a Mitutoyo MVK-H tester under various loads, ranging from

0.025 kg to 1 kg. Figure 4 shows micro hardness measured on the sample A surface with various load. It can be seen that the hardness on the untreated surface (A000) is fairly stable under a testing load of above 0.05 kg, with an average value of HV 486. After carburising, the surface hardness of the Co-Cr-Mo alloy was increased under all testing loads. Under indentation loads below 0.1 kg, surface hardness values of more than 1100 HV were obtained for the 500°C and 600°C treated samples (A500 and A600 respectively). The surface hardness values for the 400°C treated sample (A400) were not as high as those for the 500°C and 600°C treated samples, but they are still much higher than those for the untreated alloy. As the testing load increased, all the measured hardness values decreased, showing a hardness gradient with testing load and this with the indentation depth. Such a diffusion type of hardness distribution is essential in ensuring optimum performance of surface treated system, since a sudden structural, compositional, and property change at the layer/core interface may lead to catastrophic interfacial failure of the layer during service. It was also found that the edges of the Vickers indentation impressions on the carburised samples were sharp and clear. No cracks were observed around or inside the indentation impression, and there was no evidence of interfacial failure between the carburised layer and the substrate even at a higher load of 1 kg. These observations suggest that the carburised layer possesses good ductility, high toughness and high load bearing capacity.

Plasma carburised and untreated test pieces were subjected to pin (WC ball)-on-disc wear tests sliding against 8 mm WC balls at a speed of 0.03 m/s with a initial maximum Hertzian contact stress of 1500MP. Wear rate, in terms of volume loss per meter sliding distance per Newton load

( $\text{mm}^3\text{m}^{-1}\text{N}^{-1}$ ), was calculated and is shown in figure 5. As can be seen from figure 5, the wear rate of all the carburised test pieces was dramatically reduced by more than one order of magnitude as compared with the untreated test pieces.

Electrochemical potentiodynamic sweep corrosion tests were conducted at room temperature in a flat cell with Ringer's solution which contained 9 g/l sodium chloride, 0.42 g/l potassium chloride, 0.48 g/l calcium chloride and 0.2 g/l sodium bicarbonate in distilled water. The polarisation curves are shown in figure 6. As compared with the untreated test piece, the corrosion potentials of all plasma carburised test pieces were moved to more passive values, indicating improved corrosion resistance. The current densities of both the untreated and the A400 and A500 test pieces are practically the same. The A600 test piece showed a higher current density scan potential was over -0.2V.

The applicability of the present invention is demonstrated in Table 3. Treatment was carried out at 500°C for 10 hrs in a gas mixture of methane and hydrogen. Microhardness was measured on the treated sample with a Vicker's indenter at a load of 0.1kgf, indicated as HV0.1. As can be seen, all five types of Co-Cr based alloys in wrought, cast or PM/HIP form can be effectively surface hardened by applying the method of the present invention.

TABLE 3: Surface hardness of samples A to F.

Sample Number	Condition	Surface Hardness HV0.1
A	Wrought	1200
B	Wrought	1150

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C	Cast MMT)	1200
D	Cast (DEP)	1000
E	Cast (DRILL)	1240
F	PM/HIP	960

In a modification of the above dc plasma method not shown), an advanced active screen plasma technology can be used to treat articles made of Co-Cr based alloys with improved surface quality. The articles to be plasma treated are placed inside a metal screen which is connected to the cathodic potential. The worktable and the articles to be treated are placed in a floating potential or subject to a relatively lower bias voltage (e.g. -100 ~ -200V). As an example, a casting material (material D in Table 3) has been plasma treated in a active screen plasma unit and the surface hardness increased from <400HV0.1 (untreated material) to ~ 1050HV0.1 (active screen plasma treated).

**CLAIMS**

1. A method of modifying a surface characteristic of a cobalt-chromium based alloy article, comprising plasma treating the article at a temperature in the range of from 300 to 700°C and at a pressure of from 100 to 1500 Pa for 1 to 50 hours in an atmosphere comprising at least one carbon-containing gas, whereby to introduce carbon into a surface region of said article.
2. The method of claim 1, wherein the surface characteristic to be modified is one or more of hardness, wear resistance, corrosion resistance and fatigue strength.
3. The method of claim 1 or 2, wherein the article whose surface characteristic is to be modified is a medical implant, such as a joint or knee prosthesis.
4. The method of claim 3, wherein the plasma treating is carried out at a temperature in the range of from 350 to 550°C.
5. The method of claim 4, wherein the plasma treating is carried out at a temperature in the range of from 400 to 500°C.
6. The method of claim 1 or 2, wherein the article whose surface characteristic is to be modified is an engineering component, such as a knife, valve, blade or shaft.

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7. The method of claim 6, wherein the plasma treating is carried out at a temperature in the range of from 450 to 700°C
8. The method of claim 7, wherein the plasma treating is carried out at a temperature in the range of from 600 to 650°C.
9. The method of any preceding claim, wherein said treatment pressure is in the range of from 400 to 600 Pa.
10. The method of any preceding claim, wherein the duration of said treatment is in the range of from 1 to 50 hours.
11. The method of claim 10, wherein the duration of said treatment is in the range of from 5 to 30 hours.
12. The method of any preceding claim, wherein the or each carbon-containing gas is selected from a hydrocarbon, carbon dioxide and carbon monoxide.
13. The method of any preceding claim, wherein the plasma treatment is carried out in the presence of at least one unreactive gas selected from hydrogen, helium, argon or other noble gas.
14. The method of any preceding claim, wherein the plasma treatment is carried out in the presence of at least one reactive gas.
15. The method of claim 14, wherein the reactive gas is a nitrogen containing gas.

16. The method of claim 15, wherein the plasma treatment is effected at a temperature in the range of from 300 to 500°C.
17. The method of any one of claims 14 to 16, wherein said reactive gas constitutes from 0.5 to 10% by volume of the total atmosphere.
18. The method of claim 13, wherein the unreactive gas is hydrogen or a mixture of hydrogen and argon, and the carbon-containing gas is methane
19. The method of any preceding claim, wherein the or each carbon-containing gas constitutes from 0.5 to 20% by volume of the total atmosphere.
20. The method of any preceding claim, wherein said plasma treatment is effected in the absence of oxygen.
21. The method of any preceding claim which includes an article cleaning step prior to the plasma treatment to remove oxide scale.
22. The method of claim 21, wherein cleaning is effected by sputter cleaning.
23. The method of claim 21 or 22, wherein said cleaning step is effected at or below the subsequent plasma treatment temperature in an atmosphere of one or more of gases selected from hydrogen, helium, argon or other noble gas.

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24. The method of any preceding claim, wherein the article is cooled after the plasma treatment.

25. The method of claim 24, wherein the rate of cooling is from 0.1°C/min up to 1000°C/min.

26. The method of claim 24 or 25, wherein the cooling is achieved by relatively slow cooling in the plasma treating atmosphere or by relatively fast cooling by quenching in a liquid.

27. The method of any preceding claim, wherein a passivation and/or polishing step is effected after completion of the plasma treatment.

28. A surface-hardened cobalt-chromium based article producible by the method of any one of claims 1 to 27, said article characterised by having:-

- (i) a surface region comprising a supersaturated solid solution of carbon in cobalt or,
- (ii) a surface region comprising a supersaturated solid solution of carbon in cobalt and chromium carbides.

29. The article of claim 28, wherein said surface region has a thickness in the range of from 3 to 50 µm.

30. The method of any one of claims 1 to 27 or the article of claim 28 or 29, wherein the Co-Cr based alloy includes one or more other alloying

ingredients selected from molybdenum, nickel, tungsten, titanium and carbon.

31. The article of claim 30, wherein carbon is present in an amount of from 0.04 to 1.6wt%.

32. The article of claim 31, wherein the article is a medical implant and carbon is present in the range of from 0.04 to 0.4wt%.

33. The article of claim 31, wherein the article is an engineering component and carbon is present in the range of from 0.4 to 1.6wt%.

34. The article of any one of claims 28 to 33 which is a conventional hip or knee joint prostheses, a metal-on-metal advanced bone conservation prostheses, a dental implant or other implant device, a knife, blade for chemical or food processing industrials, a turbine blade, a valve or pump in the chemical and power industries, a bushing, steel mill equipment, a die, punch or mould.

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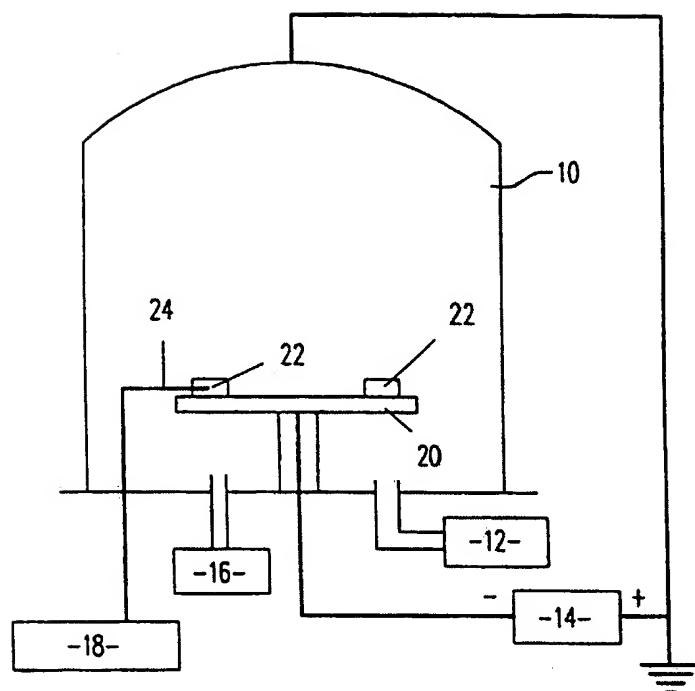


Fig.1

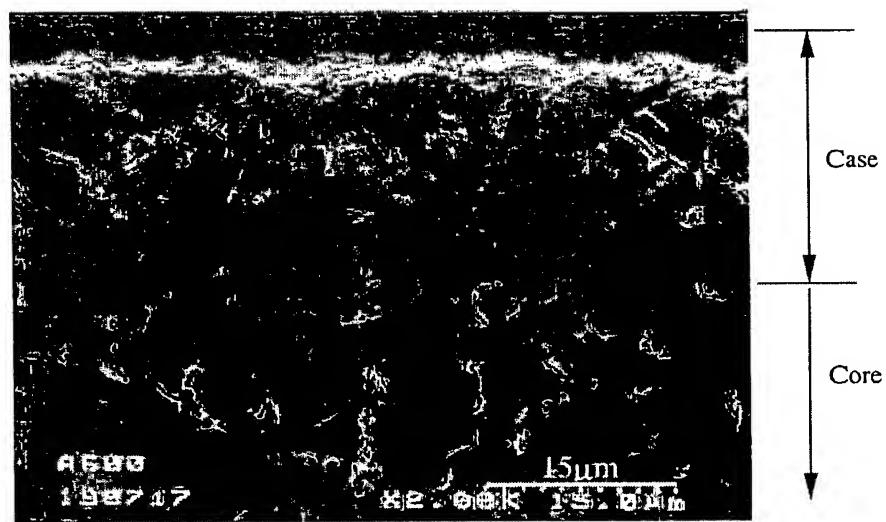


Fig 2

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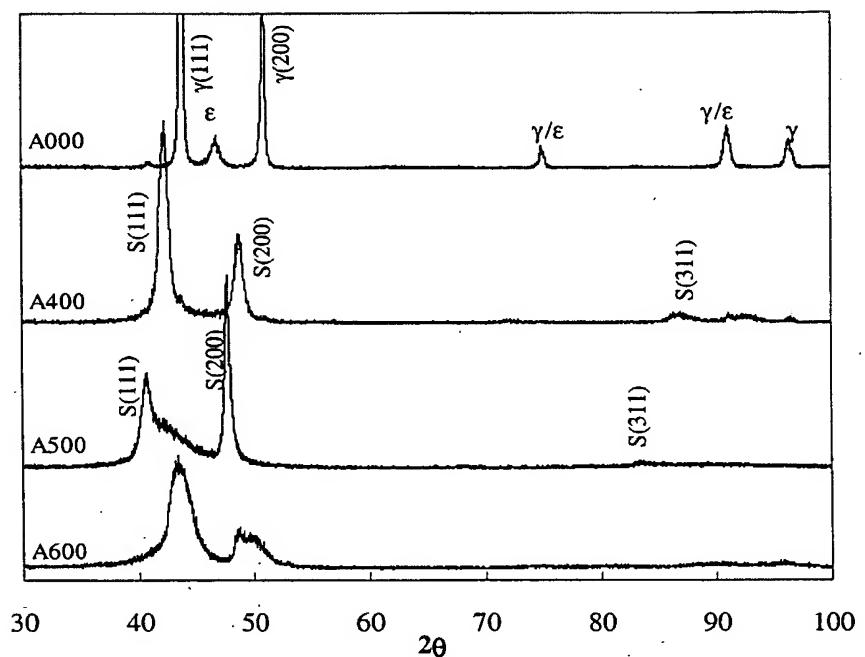


Fig.3

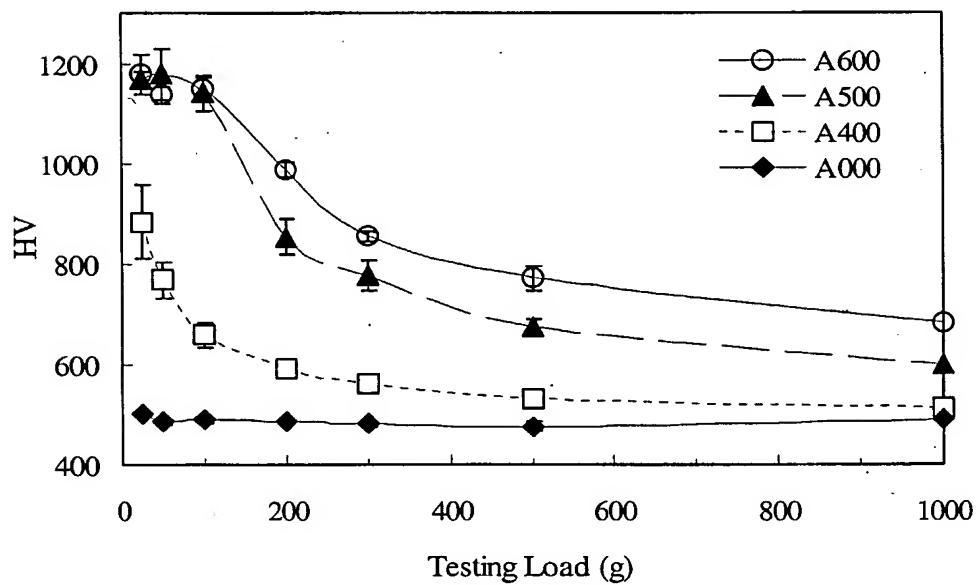


Fig. 4

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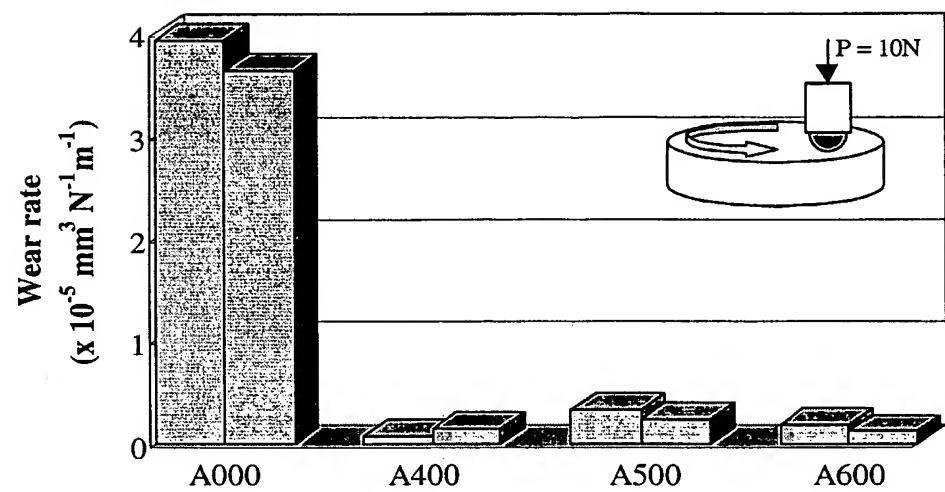


Fig.5

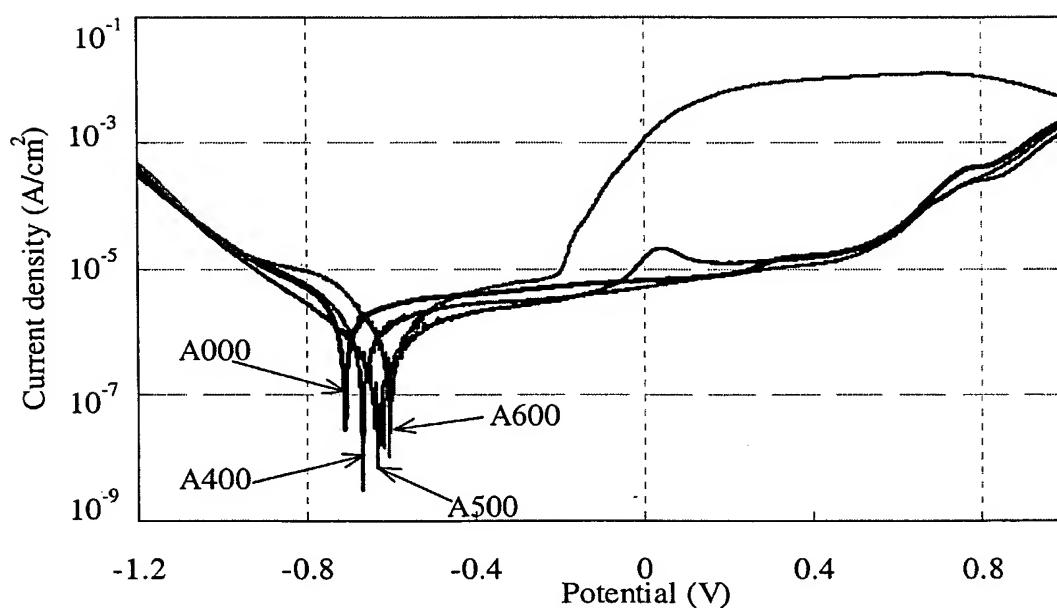


Fig. 6

# INTERNATIONAL SEARCH REPORT

Internati	Application No
PCT/GB 03/01702	

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C8/20 C23C8/36 C22C29/02 C22C19/07 A61F2/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C23C C22C A61F C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 498 302 A (DAVIDSON JAMES A) 12 March 1996 (1996-03-12) abstract column 2, line 47 - line 57 column 3, line 43 - line 53 column 4, line 9 column 5, line 40 - line 51 column 9, line 19 - line 50 --- US 5 308 412 A (OTTERSBERG WALTER H ET AL) 3 May 1994 (1994-05-03) abstract column 3, line 55 -column 4, line 19 column 5, line 14 - line 64 column 8, line 12 - line 19 --- -/--	1-34
A		1-34

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

### Special categories of cited documents :

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Date of the actual completion of the International search

8 August 2003

Date of mailing of the International search report

29/08/2003

### Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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**INTERNATIONAL SEARCH REPORT**

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**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Reference of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP 0 801 142 A (NITRUVID) 15 October 1997 (1997-10-15) the whole document ---	1-34
Y	US 4 193 825 A (KOJIMA RINZO ET AL) 18 March 1980 (1980-03-18) the whole document -----	1-34

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

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